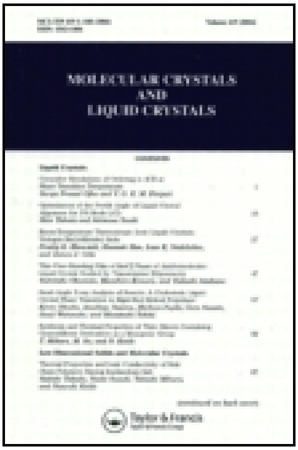

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Phase Behaviour of Cyclo-octanol up to Pressures of 300 MPa and Temperatures between 100 and 370 K

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Phase Behaviour of Cyclo-octanol up to Pressures of 300 MPa and Temperatures between 100 and 370 K

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The phase behaviour of cyclo-octanol has been studied at temperatures between 100 and 370 K and pressures up to 300 MPa with the aid of differential thermal analysis. Two new high pressure modifications (solid III and IV) have been found and accordingly two sets of triple point values: (a) the (solid I + solid II + solid III) triple point at 105 MPa and 277 K; (b) the (solid II + solid III + solid IV) triple point at 130 MPa and 278 K. Both phases solid III and IV are supposed to be orientationally disordered ("plastic") phases.

I. INTRODUCTION

The thermodynamic properties of cyclo-octanol have partly been described in recent reviews on glassy crystals.[1,2] Cyclo-octanol exhibits one plastic phase, solid I, below the melting temperature that transforms to a non-rotational form, solid II, at lower temperatures. Furthermore solid I has a strong tendency to supercool thereby forming metastable phases that have also been confirmed by dielectric measurements.[3] However, the phase behaviour at elevated pressures has not been reported in literature so far. According to previous studies[4,5] high pressure may change the polymorphism of molecular crystals considerably. It was therefore the aim of the present work to study the phase behaviour of cyclo-octanol at elevated pressures with the aid of differential thermal analysis (d.t.a.).[6]

II. EXPERIMENTAL

Details of the high pressure d.t.a. apparatus have been described elsewhere.[6,7] Cyclo-octanol was obtained from Janssen Chimica, Beerse, Belgium and purified by both distillation and gas chromatography. Thus the purity (99%) of the commercial material was increased to 99.8%. Phase transition temperatures are determined at heating rates of 2 K min^{-1}. Thermocouples of Chromel/Alumel have been calibrated against substances of known transition temperature. For both measurements and calibration the transition temperatures have been determined from the maximum of the slope of the d.t.a. trace (inflection point) after the onset of the phase transition.

The limits of experimental error for the temperature measurement is 0.5 K. High pressure is generated by compressed rare gases and measured by using Bourdon gauges (Heise, Newton Connecticut, USA). The error of the pressure reading is supposed to be less than 5 bar (1 bar = 10^5Pa).

III. RESULTS

3.1 Measurements at atmospheric pressure

Figure 1a represents d.t.a. traces obtained at atmospheric pressure showing the (solid II)-to-(solid I) transition at 264 K and the melting at 297.5 K. The very small and flat peak between these two transitions was caused by irregularities of the electronic regulating system. Preceding measurements with non-purified cyclooctanol yielded remarkably lower transition temperatures, see Table I.

The table gives also enthalpy changes that have been calculated from the peak areas after calibration against the solid state transition of cyclohexane, as well as volume changes estimated with the Clausius-Clapeyron equation. There is considerable disagreement with literature data of Dworkin *et al.*,[1] apparently caused by different degrees of purities of the samples used.

3.2 Measurements at elevated pressures

At elevated pressures additional peaks are observed in d.t.a. due to the onset of hitherto unknown phase transitions. An example is given in Figure 1b that exhibits three phase transitions. Many d.t.a. runs have been performed in order to verify the transition temperatures as a function of pressure. Thus the phase diagram has been estab-

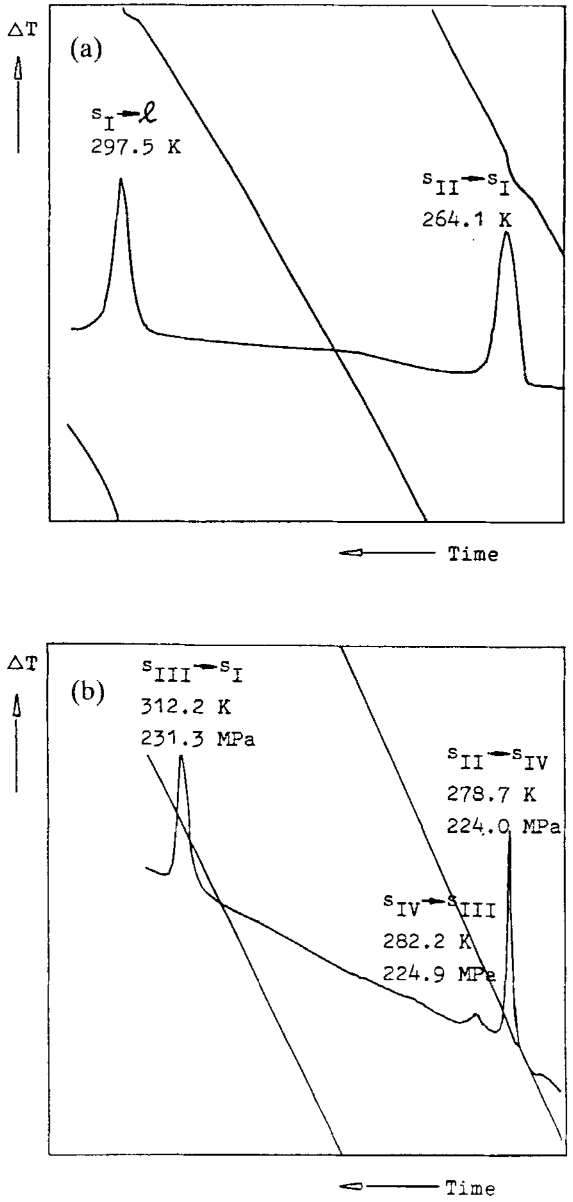

FIGURE 1 D.t.a. traces for cyclo-octanol at different pressures (a), melting and (solid I)-to-(solid II) transition at 1 bar (b), high pressure transitions with the new phases solid III and solid IV.

TABLE I

Thermodynamic properties of cyclo-octanol at 1 atm

Transition	$\frac{T}{K}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{dT/dp}{\text{K MPa}^{-1}}$	$\frac{\Delta V}{\text{cm}^3\text{mol}^{-1}}$	Author
melting	297.5	2.04	0.39	2.67	this work[a]
"	295.4	2.1			this work[b]
"	283.8	1.792			1
"	295				3
solid II/I	264	2.67	0.15	1.52	this work[a]
"	261	2.27			this work[b]
"	246.5	1.690			1
"	265				3

[a]purity = 99.8%; [b]purity = 99%

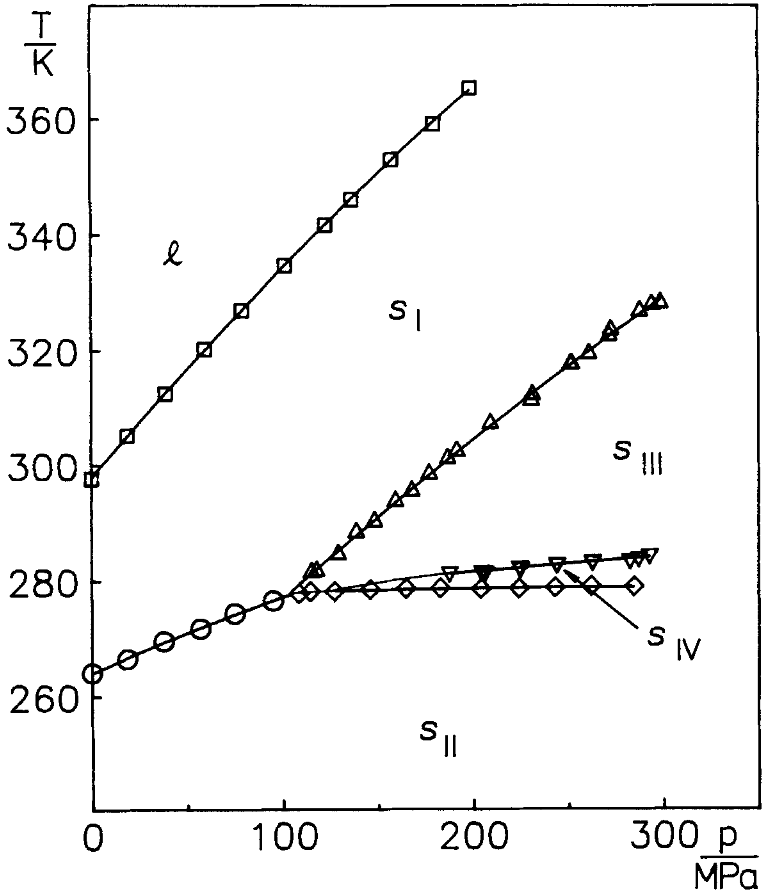

FIGURE 2 Phase diagram for cyclo-octanol, showing the new phases solid III and solid IV.

lished, revealing two new phase regions that are denoted solid III and solid IV. Accordingly there are two sets of triple-points: (a), (solid I + solid II + solid III) at 277 K and 105 MPa; and (b), (solid II + solid III + solid IV) at 278 K and 130 MPa. However, it was very difficult to determine the phase transitions accurately in the neighbourhood of the triple points because of overlapping peaks. Therefore an extrapolation of transition temperatures at higher pressures was necessary to obtain these values.

The p,T data of the phase transitions which are summarized in Table II have also been fitted to polynomials. This enabled the cal-

TABLE II

p/T—Data of the high pressure measurements of cyclo-octanol

sI–l

p/MPa	T/K
0.1	297.6
19.0	305.1
38.8	312.4
59.2	320.2
79.0	327.0
101.5	334.7
122.6	341.7
136.6	346.1
157.4	352.9
179.4	359.1
198.5	365.4

sII–sI

p/MPa	T/K
0.1	264.1
18.6	266.5
37.5	269.6
56.7	271.8
74.8	274.4
95.0	276.6

sII–sIV

p/MPa	T/K
108.5	277.9
114.5	278.2
127.2	278.7
145.8	278.5
164.6	278.7
182.6	278.8
204.0	278.6
224.0	278.7
243.0	278.9
262.0	279.1
284.4	279.0

sIII–sI

p/MPa	T/K
115.0	281.5
117.8	281.7
129.0	284.6
138.6	288.4
148.0	290.3
159.2	293.7
167.7	295.5
176.8	298.4
186.8	301.1
191.6	302.4
209.3	307.2
230.8	311.2
231.3	312.2
251.2	317.5
251.8	317.6
260.8	319.3
271.6	322.5
272.5	323.5
287.7	326.8
294.0	327.9
298.5	328.2

sIV–sIII

p/MPa	T/K
187.6	281.5
204.7	281.7
206.4	281.6
224.4	282.5
224.9	282.2
244.0	283.0
244.2	283.0
262.8	283.4
262.8	283.5
282.5	283.7
287.0	284.0
292.8	284.5

culation of the initial slopes that are also incorporated in Table I (for the evaluation of the volume changes). At elevated pressures the determination of the enthalpy change is much less accurate, mainly due to the limitations of a reasonable calibration procedure at high pressures. Approximate values are: (a), (solid III)-to-(solid I): 1.2; (b), (solid II)-to-(solid IV): 1.2; and (c), (solid IV)-to-(solid III): 0.3 kJ mol^{-1}. These values have been estimated as an average over the total pressure range in question; it is not possible to note a pressure dependence of the enthalpy change within the limits of experimental error. The small magnitude of the enthalpy change of the intermediate (solid IV)-to-(solid III) transition suggests that both phases solid III and solid IV may be "plastic phases." Indeed this has been confirmed very recently by dielectric constant measurements.[8]

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